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Notes:

- 1. Untranslatable words are replaced with asterisks (****).
- 2. Texts in the figures are not translated and shown as it is.

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H07-046973 HIRAMATSU TAKASHI IMAZU RYUJI FUKUSHIMA SADAO HAYAMIZU YASUAKI

FULL CONTENTS

[Claim(s)]

[Claim 1] The antibacterial food packaging material which contained or adhered to the cyclodexrin inclusion compound which carried out inclusion of the isothiocyanate at least.

[Claim 2] Said isothiocyanate The allyl isothiocyanate, isothiocyanic acid isoamyl, Isothiocyanic acid isobutyl, isothiocyanic acid isopropyl, isothiocyanic acid ethyl, The antibacterial food packaging material according to claim 1 which are one sort or two sorts or more of compounds chosen from the group of isothiocyanic acid nitrophenyl, phenylisothiocyanate, isothiocyanic acid butyl, the isothiocyanic acid propyl, the isothiocyanic acid benzyl, and methyl isothiocyanate.

[Claim 3] The antibacterial food packaging material according to claim 1 or 2 which is the film, the sheet, the tape, the tray, or the case where said food packaging material consists of a synthetic resin.

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the antibacterial food packaging material aiming at mildewproofing of the perishable food at the time of circulation and preservation, and a processed food, and sterilization. [0002]

[Description of the Prior Art] Much time is spent until it crosses each of perishable foods and processed foods to a consumer from a production site, and the quality deterioration by component change of food, decomposition, the development of mold, etc. pose a problem. The present condition is that do not result in decomposition, but the development of mold reduces the commodity value of food remarkably, and ** is also racking its brains for the mildewproofing procedure of the food at the time of circulation and preservation in high temperature and high humidity environment especially.

[0003] The procedure of using an ethyl alcohol emanation agent, the method of using a deoxidizer, and the method of using for the zeolite the sterilization nature mineral which installed the metal ion are conventionally examined and enforced as a method of preservation of the food by mold prevention.

[0004]

[Problem to be solved by the invention] However, although the method of using an ethyl alcohol emanation agent is suitable for a processed food, it has the problem which has a bad influence on the metabolism of a perishable food by alcoholic gas. The method of using a deoxidizer has the problem which induces the unusual metabolism of perishable foods, such as garden stuff, in super-low oxygen environment while it must pack food by a perfect sealed state when using a deoxidizer and lacks in simple nature. Moreover, the directions for use of a sterilization nature mineral are restrained remarkably and the procedure of using a sterilization nature mineral does not have them as a method of preservation of food to demonstrate an effect only in a contact surface with a sterilization nature mineral. [enough] Although the disinfection and the mildewproofing material which infiltrated into the silica gel the isothiocyanate which furthermore has a ring in a JP,52-1023,A number Description are proposed, in being unable to maintain an antibacterial effect for a long period of time, but fabricating on a sheet etc. and using for a packaging material, a problem is in a heat-resisting property and it spoils an antibacterial effect.

[0005] the antibacterial food packaging material which this invention did not have [food packaging material] a bad influence over food at large by using the isothiocyanate which consists of a volatile vegetable extraction component in view of this present condition, but mildewproofing and sterilization over the long period of time of food were aimed at [food packaging material], and made the outstanding heat-resisting property provide -- it is going to provide -- it is a thing.

[0006]

[Means for solving problem] The thing which generally generate this invention persons for food wholeheartedly as a result of research and for which it molds and bacteria are increased under high humidity, Moreover, the thing for which the educt from a natural plant, especially isothiocyanate have an effect in mildewproofing of food, and sterilization, and it moreover has food safety when isothiocyanate is what is obtained from a natural plant, [it is unstable, if said isothiocyanate still remains as it is, light, heat air, water, etc. decompose gradually and an antibacterial effect is lost, but] By carrying out inclusion to cyclodexrin and considering it as a cyclodexrin inclusion compound In the usual dry state, it is fixed to cyclodexrin, and said isothiocyanate hardly volatilizes, but discharge volatilization of the isothiocyanate is carried out from cyclodexrin under high humidity, By carrying out inclusion of the isothiocyanate still more nearly lacking in a heat-resisting property to cyclodexrin, can also make a heat-resisting property give, therefore knead this cyclodexrin inclusion compound to a synthetic resin, and [a film, a sheet, a tape, a tray, or a case / carry out heating molding or] Learning is carried out from the antibacterial effect of isothiocyanate not being spoiled, even if it carries out the ustulation after printing and applying at a film etc. printing ink and the paint having contained the cyclodexrin inclusion compound etc., and it comes to complete this

[0007] That is, the antibacterial food packaging material of this invention is characterized

by containing or adhering to the cyclodexrin inclusion compound which carried out inclusion of the isothiocyanate at least.

[0008] This invention persons conducted the following experiments, in order to investigate whether what kind of thing molds among the educts from a natural plant first, and it has the suppression (antibacterial properties) effect of proliferation.

[0009] The agar (PDA culture medium) which inoculated various kinds of mold (A. niger, Fsarium, Geotrichum Candidum, Alternaria) as the experiment 1 experiment procedure on condition of the following experimental plots [essential oil / vegetable extraction] Glass hermetic containers (4000 cc) were enclosed, it cultivated for four days at 28 degrees C, and the result was shown in Table 1.

Experimental plot 1 0.02g of Japanese horseradish extracted oil use.

Experimental plot 2 0.04g of garlic extracted oil use.

Experimental plot 3 0.04g of onion extracted oil use.

Control plot What does not use vegetable extracted oil. [0010]

[Table 1]

菌 種	試 験 区		対照区	
PS 1#.	1	2	3	A JARICA
A. niger		+	+	++
Fsarium	_	+	+	++
G. Candidum		+	+	++
Alternaria	_	+	+	++

++ ……抗菌効果がまったくない

+ …… // ほとんどない

士 …… 〃 ややある

_ // ある

ーー …… 〃 十分ある

[0011] As a result, the antibacterial effect has been notably checked to the Japanese horseradish extracted oil of the blank test division 1. The active ingredient of Japanese horseradish extracted oil is isothiocyanate, therefore this invention uses isothiocyanate as antibacteria medicine. Isothiocyanate is a compound expressed with a general formula by ** 1. The allyl isothiocyanate, isothiocyanic acid isoamyl, isothiocyanic acid isobutyl, Isothiocyanic acid isopropyl, isothiocyanic acid ethyl, isothiocyanic acid nitrophenyl, Phenylisothiocyanate, isothiocyanic acid butyl, the isothiocyanic acid propyl, the isothiocyanic acid benzyl, methyl isothiocyanate, etc. are used suitably, and especially the allyl isothiocyanate is more suitably used from demonstrating a clear effect. In addition, you may be used, blending with said isothiocyanate the terpene which has an antibacterial effect. ** -- it is for the antibacterial effect of an antibacterial effect of isothiocyanate and the terpene to improve further conjointly, if made like. As this

terpene, hydrocarbon, such as an alpha pinene, l-limonene, d-limonene, monoterpenes, and sesquiterpenes, terpene alcohol, terpene aldehyde, etc. are used suitably. [0012]

[Chemical formula 1]

R - N = C = S

[0013] However, if isothiocyanate remains as it is, it is unstable, light, heat, air, water, etc. decompose gradually, and an antibacterial effect is lost.

[0014] Then, since the above-mentioned isothiocyanate is saved at a long period of time, inclusion is carried out to cyclodexrin and it is used as a cyclodexrin inclusion compound. Moreover, although isothiocyanate is fixed to cyclodexrin by the usual dry state by carrying out inclusion of the isothiocyanate to cyclodexrin in this way and it hardly volatilizes, under high humidity, it volatilizes for the hydrophobicity which cyclodexrin has. Therefore, while making antibacterial properties provide by making said cyclodexrin inclusion compound contain or adhere in this invention antibacterialproperties food packaging material Isothiocyanate is not volatilized and it is made to make it volatilize under high humidity suitable for proliferation of mold or bacteria in the usual dry state unsuitable for proliferation of mold or bacteria. In addition, [inside the packaging material, kneading unification is carried out, and the cyclodexrin inclusion compound may contain, and The surface may adhere by printing, paint, etc., and in short, if the cyclodexrin inclusion compound exists in the inside and the surface of the packaging material, although it will exist how especially, it will not be limited. [0015] As this invention antibacterial-properties food packaging material, the film, the sheet, the tape, tray, or case which consists of a synthetic resin is desirable, and this invention effect can be used most effectively. Namely, since isothiocyanate lacking in a heat-resisting property can be made to possess a heat-resisting property by carrying out inclusion of the isothiocyanate to cyclodexrin Knead this cyclodexrin inclusion compound to a synthetic resin, and A film, Heating molding is carried out, or it applies, and printing and after making it adhere, the ustulation of printing ink and the paint having contained the cyclodexrin inclusion compound is carried out to said film etc. at a sheet, a tape, a tray, or a case, pass a heating step in the process which manufactures this invention packaging material -- [without spoiling the antibacterial effect of isothiocyanate / the food packaging material which has antibacterial properties / obtain and] even if it is Moreover, even if it performs post processing included heating processing so that thermoforming may be carried out in order to make saccate etc. this invention packaging material which consists of a film, for example, it is because the antibacterial effect of isothiocyanate is not spoiled. [0016]

[Function] If food is packed with the antibacterial food packaging material by this invention, generally will mold and isothiocyanate will not volatilize from cyclodexrin in the usual dry state which bacteria do not increase. While being able to save stably, without spoiling the antibacterial effect as antibacteria medicine, it can mold, isothiocyanate can volatilize from cyclodexrin under high humidity suitable for bacterial proliferation, and an antibacterial effect can be demonstrated effectively. Moreover, since the heat-resisting property is given by carrying out inclusion of the isothiocyanate inferior to a heat-resisting property to cyclodexrin, an antibacterial effect is not spoiled even if

this invention antibacterial-properties food packaging material performs heating processing.

[0017]

[Working example] Hereafter, the examination by this invention work example etc. is done, and the effect of this invention is shown.

[0018] Like examination 1 drawing 1, a petri dish 1 is filled with the potato dextrose agar 21, and is solidified, and it is 1x106 to the surface of the agar 21. It inverted, after carrying out the smear of the fungus liquid 31 of the FUZARYUUMU group which is a kind of the mold prepared to ** and covering with the lid 4 of a petri dish 1, and it cultivated in the temperature of 25 degrees C, and 75% of humidity atmosphere. At this time, like the following experimental plots 1-9, isothiocyanate 5 was made to exist, the mildew resistant effect was observed seven days, 14 days, and 21 days afterward, and that result was shown in Table 2.

Experimental plot 1 -- 0.04 cc of undiluted solutions which used the allyl isothiocyanate as the main ingredients are dropped at the inside of a lid 4.

Experimental plot 2 -- 0.2g of cyclodexrin inclusion compounds of the same undiluted solution as an experimental plot 1 are neglected in the inside of a lid 4.

Experimental plot 3 -- 0.4g of polyethylene pellet mold goods containing the same cyclodexrin inclusion compound as an experimental plot 2 are neglected in the inside of a lid 4.

Experimental plot 4 -- The film (0.5% of allyl-isothiocyanate content) produced with the polyethylene pellet mold goods containing the same cyclodexrin inclusion compound as an experimental plot 3 is used instead of a lid 4 (<u>drawing 2</u>).

Experimental plot 5 -- 0.04 cc of undiluted solutions which used isothiocyanic acid isobutyl as the main ingredients are dropped at the inside of a lid 4.

Experimental plot 6 -- 0.04 cc of undiluted solutions which used isothiocyanic acid ethyl as the main ingredients are dropped at the inside of a lid 4.

Experimental plot 7 -- 0.04 cc of undiluted solutions which used the isothiocyanic acid benzyl as the main ingredients are dropped at the inside of a lid 4.

Experimental plot 8 -- 0.04 cc of undiluted solutions which used the isothiocyanic acid propyl as the main ingredients are dropped at the inside of a lid 4.

Experimental plot 9 -- 0.04 cc of undiluted solutions which used the isothiocyanic acid benzyl as the main ingredients, and 0.04 cc of undiluted solutions which used the alpha pinene as the main ingredients are dropped at the inside of a lid 4.

In addition, in the lid 4, what nothing processes was made into the control plot, and it was shown according to Table 2.

[0019]

[Table 2]

		防	黴 効	果
		7日後	1.4日後	2 1 日後
	1	0	0	0
試	2	0	©	©
	3	0	©	©
i	4	©	0	0
験	5	0	0	
	6	0	0	0
	7	0	0	0
区	8	0	0	0
	9	©	©	0
対	照区	×	×	×

◎…徽発生せず

○…黴やや発生

×····徵発生

[0020] After filling a petri dish 1 with the fungus liquid 32 containing the DEZOKISHIKO rate agar 22 and a coli form group, solidifying it and covering with the lid 4 of a petri dish 1 like examination 2 <u>drawing 1</u>, pour culture was carried out at the temperature of 35 degrees C. At this time, like the following experimental plots 1-7, isothiocyanate 5 was made to exist, the antibacterial effect was observed seven days, 14 days, and 21 days afterward, and that result was shown in Table 3.

Experimental plot 1 -- 0.04 cc of undiluted solutions which used the allyl isothiocyanate as the main ingredients are dropped at the inside of a lid 4.

Experimental plot 2 -- 0.2g of cyclodexrin inclusion compounds of the same undiluted solution as an experimental plot 1 are neglected in the inside of a lid 4.

Experimental plot 3 -- 0.4g of polyethylene pellet mold goods containing the same cyclodexrin inclusion compound as an experimental plot 2 are neglected in the inside of a lid 4.

Experimental plot 4 -- The film (0.5%) of allyl-isothiocyanate content) produced with the polyethylene pellet mold goods containing the same cyclodexrin inclusion compound as an experimental plot 3 is used instead of a lid 4 (drawing 2).

Experimental plot 5 -- 0.04 cc of undiluted solutions which used isothiocyanic acid isobutyl as the main ingredients are dropped at the inside of a lid 4.

Experimental plot 6 -- 0.04 cc of undiluted solutions which used isothiocyanic acid ethyl as the main ingredients are dropped at the inside of a lid 4.

Experimental plot 7 -- 0.04 cc of undiluted solutions which used the isothiocyanic acid benzyl as the main ingredients, and 0.04 cc of undiluted solutions which used the alpha

pinene as the main ingredients are dropped at the inside of a lid 4. In addition, in the lid 4, what nothing processes was made into the control plot, and it was shown according to Table 3.

[0021]

[Table 3]

_	[14616-5]					
		抗	菌 効	果		
•		7 日後	14日後	2 1 日後		
	1	0	©	0		
絬	2	©	0	0		
	3	0	©	0		
験	4	0	0	0		
	5	©	0	0		
X	6	0	0	0		
	7	©	©	©		
対	照区	×	×	×		

◎…集落形成せず

○…集落やや形成

×…集落形成

[0022] [the film produced with the polyethylene pellet mold goods and these polyethylene pellet mold goods of an experimental plot 4 which contain the cyclodexrin inclusion compound of the allyl isothiocyanate of the experimental plot 3 which is this invention work example from the result of examination 1 and examination 2] In spite of carrying out heating molding in the manufacture process, it turns out that it has the same antibacterial effect to the FUZARYUUMU group and colibacillus which are a kind of mold as all used the very thing which blended the isothiocyanate itself or the terpene. [0023] Moreover, the following experiments were conducted in order to investigate the character of the cyclodexrin inclusion compound of the allyl isothiocyanate. [0024] The cyclodexrin to which saturation content inclusion of the experiment 2 allyl isothiocyanate was carried out was enclosed with glass hermetic containers (4000 cc), and the allyl-isothiocyanate gas concentration in the container 24 hours after 30 degrees C was measured in the state of a dry state (60% of humidity), and high humidity (95% of humidity). Moreover, the diatom earth of the mineral generally well used as a carrier for comparison is made to carry out saturation content support of the allyl isothiocyanate, the same experiment is performed to it, and the result is shown in it at drawing 3. [0025] As opposed to the allyl isothiocyanate which carried out inclusion to cyclodexrin from the result of <u>drawing 3</u> hardly volatilizing in the state of the usual humidity It turns out that it is volatilizing effectively under high humidity, therefore it generally molds,

and it excels in preservation stability, molds in the usual dry state which bacteria do not increase, and volatilizes effectively at the time of high humidity required for bacterial proliferation, and an antibacterial effect can be demonstrated. However, it turns out that it is volatilizing regardless of humidity when a diatom earth is made to support, and it is inferior to long-term preservability.

[0026] In order to investigate the thermal stability of the cyclodexrin to which saturation content inclusion of the experiment 3 allyl isothiocyanate was carried out, it heats at the temperature of 150 degrees C - 190 degrees C for 10 minutes - 30 minutes, and the retention of the amount initial value of volatilization is investigated, and the result is shown in $\underline{\text{drawing 4}}$. In addition, the result at the time of making a saturation content diatom earth support the allyl isothiocyanate, and heating it for 5 minutes at 150 degrees C is also doubled, and it writes together to $\underline{\text{drawing 4}}$.

[0027] If inclusion is carried out to cyclodexrin from this result even if it is the allyl isothiocyanate lacking in a heat-resisting property, even if it will heat at 190 degrees C for 30 minutes, the amount initial value retention of volatilization is as high as 80%, and it turns out that it has a heat-resisting property. This kneads this cyclodexrin inclusion compound to a synthetic resin, and A film, Heating molding is carried out, or it applies, and printing and after making it adhere, the ustulation of printing ink and the paint having contained the cyclodexrin inclusion compound is carried out to said film etc. at a sheet, a tape, a tray, or a case, pass a heating step in the process which manufactures this invention packaging material -- [without spoiling the antibacterial effect of isothiocyanate, even if it is] Even if it performs post processing included heating processing so that thermoforming may be carried out in order to make saccate etc. this invention packaging material which the food packaging material which has antibacterial properties is obtained, and consists of a film, the thing for which the antibacterial effect of isothiocyanate is spoiled and as for which things are not is meant.

[0028] In addition, if not only a vegetable extraction component but safety is accepted, these synthetics can use isothiocyanate similarly.
[0029]

[Effect of the Invention] As explained in full detail above, [this invention antibacterialproperties food packaging material | Since the cyclodexrin inclusion compound of isothiocyanate is made to contain or adhere In the usual dry state unsuitable for proliferation of mold and bacteria, it is fixed to cyclodexrin and isothiocyanate hardly volatilizes. It molds, while excelling in the preservation stability as antibacteria medicine extremely, and under high humidity suitable for bacterial proliferation, isothiocyanate volatilizes and an antibacterial effect can be demonstrated effectively. Therefore, if this invention antibacterial-properties food packaging material is used for food, the mold of the food at the time of circulation preservation and bacterial proliferation are controlled, and it can provide for a consumer, without reducing the commodity value of food. And when using the extraction component from a natural plant, there is food safety. [0030] Moreover, since an antibacterial effect is not spoiled even if a heat-resisting property is given and it heats by carrying out inclusion of the isothiocyanate inferior to a heat-resisting property to cyclodexrin, this invention antibacterial-properties food packaging material is applied suitably for the food packaging material of all uses manufactured by performing heating processing.

[Brief Description of the Drawings]

[Drawing 1] It is the explanatory view showing the test method which investigates the antibacterial effect of this invention.

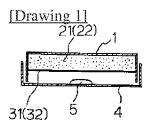
[Drawing 2] It is the explanatory view showing the test method which investigates the antibacterial effect of this invention.

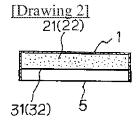
[Drawing 3] It is the graph which shows desiccation of the cyclodexrin inclusion compound of the allyl isothiocyanate, and the influence of a damp or wet condition.

[Drawing 4] It is the graph which shows the thermal influence of the cyclodexrin inclusion compound of the allyl isothiocyanate.

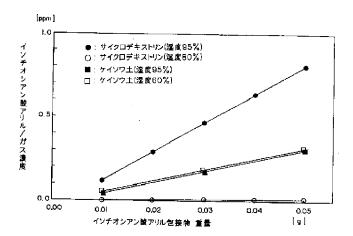
[Explanations of letters or numerals]

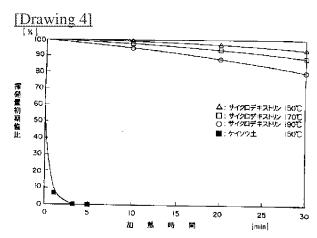
- 1 Petri Dish
- 21 Potato Dextrose Agar
- 22 DEZOKISHIKO Rate Agar
- 31 Fungus Liquid of FUZARYUUMU Group
- 32 Fungus Liquid Containing Coli Form Group
- 4 Lid
- 5 Isothiocyanate





[Drawing 3]





[Translation done.]